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Actions of Alcohols on  
Mesoxalic Ester

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# ACTION OF ALCOHOLS ON MESOXALIC ESTER

BY

F. GRACE C. SPENCER

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## THESIS

For the Degree of Bachelor of Science

in Chemistry

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College of Science

University of Illinois

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PRESENTED JUNE, 1908

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

F. Grace C. Spencer

ENTITLED Action of the Alcohols on Mesoxalic Ester.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

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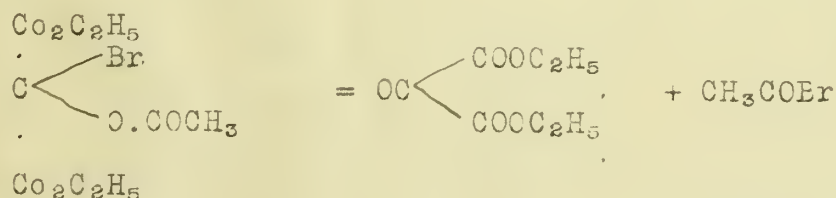






# ACTION OF THE ALCOHOLS ON MESOXALIC ESTER.

Methyl oxomalonate  $O = C \begin{cases} COCCH_3 \\ COOCH_3 \end{cases}$  was prepared by R. Anschutz and E. Parlato<sup>(1)</sup> by the distillation of the ethyl dihydroxymalonate under reduced pressure and passing the vapors through a tube containing phosphorus pentoxide. This did not give a water free product. They also prepared it by distillation of acetyl bromide under reduced pressure. The acetyl bromide breaks up according to this reaction.



But they were not able to separate the two liquids and obtain the pure ketone oil.

Methyl mesoxalate  $\begin{array}{c} HO \\ HC \end{array} > C < \begin{cases} COCCH_3 \\ COOCH_3 \end{cases}$  was obtained by Tarnoski (2) by the action of nitrous anhydride on

(1) Ber. d. Deutsch. Chem. Vol. 25, (2), p. 3615

(2) Thesis by F. T. Tarnoski, U. of I., 1907.

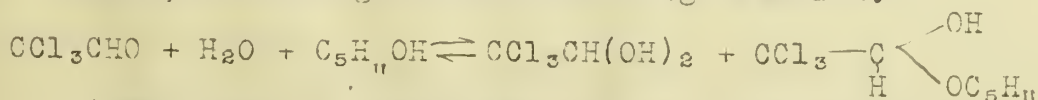


methyl malonate, according to the method discovered by Curtiss (1) for making the ethyl ester.

Tarnoski prepared the ketone oil by distillation of the methyl dihydroxymalonate under reduced pressure. It distilled at a constant temperature of 100° (uncorrected) and a pressure of 20 m.m. The oil was saturated with the dihydroxymalonate.

Owing to the reactivity of the carbonyl group, the ketone ester was difficult to obtain pure. The hydrated compound was mixed with various strong dehydrating agents, such as zinc-chloride, barium oxide, and phosphorus pentoxide, and distilled. The action of phosphorus pentoxide was found to be the best, giving a yield of 92 per cent of the pure anhydrous methyl oxomalonate.

F. Kuntz (2) has succeeded in adding several members of the alcohol series on the carbonyl group of the chloral. Alcohol acts upon the chloral hydrate until an equilibrium mixture is obtained, according to the following reaction.



A Hantzsch (3) has succeeded in combining chloral and urethane and obtaining a condensation product of this

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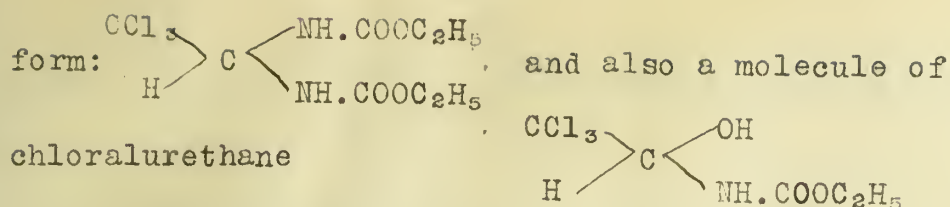
(1) Amer. Chem. Jour. Vol. 72, No. 6, June, 1905.

(2) Chemisches Central-blatt, April 22, 1908, p.1560

(3) Ber. d. Deutsch. Chem. Vol. 27, p. 1248.







As we studied particularly the reactions of alcohol and the haloid<sup>acid</sup> addition products of the ketone oil, a brief resumé of the work will be given.

Various reactions were tried on the pure methyl oxomalonate. The action of methyl, ethyl and propyl alcohols were first tested. In the case of the ethyl alcohol a crystalline body, <sup>methyl-</sup> ~~of~~ ethoxytartronate was formed. The reaction products of methyl and propyl alcohols with methyl oxomalonate were thick, glycerine-like oils.

The action of ammonia, aniline and urethane on the ketone oil was also tested. And, like the alcohols, they formed addition products on the carbonyl group. The intensity of reaction varying directly with the positive character of the substituted radical in the ammonia molecule.

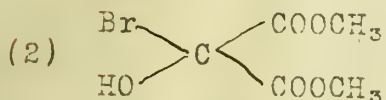
The action of dry hydrochloric and hydrobromic acid gases on the ketone ester was tested. Even here, with these strongly negative compounds, addition also takes place on the carbonyl group, forming substances which appear to be the first representatives of a new class of organic compounds, namely, the alpha,alpha,chlor-hydroxy esters. Substances of this empirical formula are possible as oxonium compounds, such as those made by Baeyer (1).

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(1) Chemisches Central-blatt, 1901 (2) p 973-976; p. 1249



That our addition products have the formula:



and are not oxonium compounds is shown by the reactions:

1. With water, in which the chlorine is replaced by the hydroxyl group, the latter being combined with carbon, giving methyl dihydroxymalonate.

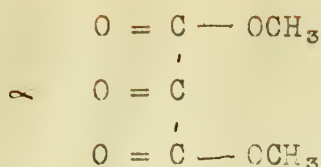
2. The action of alcohol yields methyl ethoxytartronate in which the ethoxy group has displaced the chlorine upon the carbon.

3. The best proof for the structure assigned to these addition products rests upon the fact that in their formation, the green color of the ketone ester is entirely discharged, forming colorless products. This is true of all the addition products of the ketone ester thus far studied.

According to the theory of Stewart and Baly recently proposed, to explain the cause of color in all organic compounds, this phenomenon depends upon the rapid oscillatory vibrations of adjacent supplementary valencies, and is of such a character as to produce ether vibrations of the order of those which give us the spectrum colors. In this ketone ester this phenomenon depends upon the alpha carbonyl group .

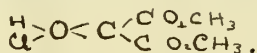






This is shown by the fact that when the free central carbonyl group has its valences saturated, as it does in these addition reactions, the color at once vanishes, and returns again as soon as the added particles are dissociated, regenerating a double bond.

For this reason the discharge of color on the addition of hydrochloric or hydrobromic acid on the ketone ester shows that the reaction has eliminated this chromophore group and that the compound is, therefore, not of the oxonium structure.



## EXPERIMENTAL

### PREPARATION OF KETONE ESTER.

(a) BARIUM OXIDE ON METHYL DIHYDROXYMALONATE: Ten grams of methyl dihydroxymalonate were mixed with eighteen grams of barium oxide, (Barium oxide from Sargent Company was in bottles imperfectly sealed), and distilled under reduced pressure. The ketone produced was not pure and the yield was very low.

(b) ACTION OF ZINC CHLORIDE ON METHYL DIHYDROXYMALONATE: Ten grams of methyl dihydroxymalonate were mixed with an excess quantity of zinc chloride and allowed to stand over



night in a separatory funnel. The substance was heated the next day and when the temperature reached  $70^{\circ}$ , it became slightly tinged with green. It was boiled for two hours, then the residue was run off and the following day the product was distilled under reduced pressure. The yield of pure oil was very small.

(c) ACTION OF PHOSPHORUS PENTOXIDE ON METHYL DIHYDROXYMALONATE: Twenty-five grams of pure methyl dihydroxymalonate were mixed with twenty-two grams of phosphorus pentoxide in a distilling bulb and allowed to stand air tight for two hours. At the end of that time it was a faint yellow porous mass from which a quantity of green-yellow liquid had separated. The pure ketone ester was then obtained by fractional distillation under reduced pressure. The fractions are not necessary, however, because when the substance is properly mixed, it all distills pure at a constant temperature of  $106^{\circ}$  (uncorrected) and 40 m.m. pressure. The mixture froths on heating and the green oil rises to the surface of the mass. After the ketone ceased to distill, the mixture in the flask finally turned to a thick, black, gummy mass.

PROPERTIES OF PURE KETONE ESTER: The pure methyl oxomalonate is a grass-green oil, Sp. gr. 1.24. It possesses a remarkable reactivity on the carbonyl group, which accounts for the rapid change back into the hydrated form when distilled. It reacts with ammonia and its derivatives, with phenyl amine and various other reagents.





# ACTION OF ALCOHOLS ON THE KETONE ESTER.

ETHYL ALCOHOL ON KETONE ESTER: One and four-tenths cc. of absolute alcohol was added from a pipette to four and two-tenths cc. (molecular quantities) of ketone ester. The temperature rose to 83°. It was then chilled and the green color slowly disappeared, leaving a faintly tinted oily liquid. Two or three drops of alcohol were added and the color entirely disappeared. The mixture, now a thick, glycerine-like oil was placed in a freezing mixture. It crystallized rapidly in balls of radiating needles and generated heat. The crystals were practically dry and hard and were purified by recrystallization from absolute alcohol, filtered on a pump, and washed with cold alcohol several times.

## ANALYSIS:

Calculated for	$\begin{array}{c} \text{C}_2\text{H}_5\text{O} \\ \text{HO} \end{array} > \text{C} \begin{array}{l} \diagup \text{COOCH}_3 \\ \diagdown \text{COOCH}_3 \end{array}$	
		Found.
		1. 2.
C = 43.75	C = 43.65	43.52
H = 6.25	H = 6.35	6.22

PROPERTIES: The methyl ethoxytartronate melts at 58°. It crystallizes in balls of radiating needles. It is easily soluble in benzene, ether, acetone, chloroform, absolute alcohol, amyl alcohol, methyl alcohol and water; fairly soluble in carbon tetrachloride; and difficultly soluble in cold ligroin.



METHYL ALCOHOL ON THE KETONE OIL: 1.6 grams of methyl alcohol were added to 4.8 cc. of ketone oil, the temperature rose to  $85^{\circ}$ . When the mixture was cooled, it became a thick, slightly green oil, which became colorless when ten per cent excess of alcohol was added, and allowed to stand in a freezing mixture for a few minutes.

The color showed a slight dissociation, which was due to uncombined ketone, which, by excess of alcohol, was completely changed into the methoxy body.

There was no indication of crystallization. When the substance was allowed to stand in the air a crystalline body, which was found to be methyl dihydroxymalonate, was formed. This shows the substance to be unstable and that it is readily changed by the moisture of the air. When the substance is boiled a green solution results, showing that dissociation takes place; and, on cooling, the color partially discharges, showing a reassociation of the alcohol and ketone.

PROPYL ALCOHOL ON THE KETONE ESTER: 1.4 cc. of propyl alcohol was added to 2.2 cc. of ketone ester, (molecular quantities), the temperature rose rapidly to  $75^{\circ}$  and all the color disappeared. No crystalline form was shown and the substance was converted into the methyl dihydroxymalonate when exposed to the air, the same as the methyl addition product.

The methyl and propyl alcohol addition products are both colorless, glycerine-like oils, which dissociate





when heated, and, hence, cannot be purified by distillation and, as they cannot be crystallized, it is impossible to obtain them in the pure state.

AMMONIA GAS ON THE KETONE ESTER: Two volumes of dry ether were added to a small quantity of the ketone oil and placed in an ice mixture. Dry ammonia gas was run through the mixture. There was apparently no action for ten minutes, then the mixture passed to a white, solid crystalline mass which changed to a faint yellow in the air. The substance, before being purified, melted at  $155^{\circ}$  and changed to a cherry-red liquid. It recrystallized in long needles from alcohol, and in rhombohedral plates truncated at the ends when crystallized from ether.

The crude ammonia addition product is easily soluble in cold water; insoluble in acetic ether, and slightly soluble in absolute alcohol, benzene, acetone, chloroform and dry ether. It leaves an insoluble residue from benzene. This was not analyzed because of lack of time.

THE ACTION OF ANILINE ON THE KETONE ESTER: One molecule of aniline dissolved in an equal quantity of sodium dry ether was added drop by drop to one molecule of ketone ester. The reaction was so intense that the aniline caused a hissing sound when it combined with the ketone and some of the ether was expelled. The substance was placed in a freezing mixture. After four minutes, the substance began to crystallize in little balls of needles and then went completely solid into a hard, yellowish-white crystalline mass which, on breaking up,



looked like damp meal. It was then filtered and washed carefully with dry ether. Recrystallized from 15 cc. of the same solvent, filtered on a pump and well washed. The yield was quantitative and it showed a melting point of 102°.

ANALYSIS:

Calculated for	$\text{C}_6\text{H}_5$	$\begin{array}{c} \text{NH} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{HO} \end{array}$	$\begin{array}{c} \text{COOCH}_3 \\ \diagup \\ \text{C} \\ \diagdown \\ \text{COOCH}_3 \end{array}$	
C = 55.23				Found
H = 5.44				C = 55.28
N = 5.88				H = 5.54
				N = 6.22

PROPERTIES: The anilinetartronic ester melts at 102° and is a pure white crystalline substance. It is easily soluble in <sup>hot</sup> methyl alcohol, acetone, and hot ethyl alcohol; fairly soluble in cold ethyl alcohol, benzene, and cold methyl alcohol; difficultly soluble in water and carbon tetrachloride, ligroin, and carbon bisulphide. Hydrochloric acid dissolves it to a colorless liquid. Nitric acid forms a deep blue colored liquid which, when diluted with water, turns to a light green, after discharging the blue color. Hot water dissociates it and gives the dihydroxy body. When the product cools, the aniline separates out as an emulsion of characteristic odor.

1. 8 cc anilinetartronic ester was mixed with .672 cc. of aniline in an Erlenmeyer flask and heated in a metal bath for one hour and a half. The temperature was gradually raised to 190° and kept constant. There was no apparent





solution at first, the substance slowly dissolved and when heated, a thin film of water formed on the inside of the flask. After an hour, the product was a deep dark red, dye-like oil. This test was made in order to ascertain whether or not the dianilinomalonic ester could be formed.

Aniline was added to a small portion of the anilino tartronic ester in a test tube and a crude product having a melting point of  $110^{\circ}$  was obtained.

A small quantity of the anilino body was mixed with phosphorus pentachloride<sup>in</sup> a tightly stoppered tube which had a fine exit. The mixture soon turned yellow and pasty; heat was generated and it becomes a canary yellow color. When the substance was warmed to  $40-50^{\circ}$ , it liquifies with a rapid evolution of non-combustible gas which was not methyl chloride, but hydrochloric acid. A colorless liquid distills up the tube. The residue is a honey-like oil which is apparently not soluble in ether.

URETHANE ON THE KETONE ESTER: .6 cc. of the ester was added to .45 gram of urethane. The urethane dissolved, producing cold, but with no apparent change. When it has all dissolved, the temperature rose to about  $50^{\circ}$ . It then became a glycerine-like syrup and crystals started to form in salt-like cubes. This was an addition product which was not analyzed because of lack of time.





# ACTION OF HALOID ACIDS ON THE KETONE ESTER.

THE ACTION OF HYDROCHLORIC ACID GAS: A weighed flask containing 1.208 grams of ketone ester was chilled for a few minutes. Hydrochloric acid gas, dried by running through concentrated sulphuric acid, was passed into the flask containing the pure ketone, and great care was taken to keep the moisture out of the flask during the process. In about five minutes the green oil became a nearly colorless, glycerine-like syrup. The substance was then placed in a freezing mixture and it began to crystallize in radiating balls with the liquid apparently boiling at the edge of the crystal as the excess of gas was expelled. The crystals were dry and pure white in color. The reaction is perfectly quantitative, - exactly one molecule of hydrochloric acid was added, as shown by the increased weight of the flask and by a chlorine determination, as follows:

## (1) Addition of hydrochloric acid gas.

Calculated for	$\begin{array}{c} \text{Cl} \diagup \\ \text{C} \\ \text{HO} \diagdown \end{array} \begin{array}{l} \diagdown \text{COOCH}_3 \\ \diagup \text{COOCH}_3 \end{array}$	
Per cent		Found
Cl. ---	- 19.43	19.25

## (2) Silver chloride determination.

Calculated for	$\begin{array}{c} \text{Cl} \diagup \\ \text{C} \\ \text{HO} \diagdown \end{array} \begin{array}{l} \diagdown \text{COOCH}_3 \\ \diagup \text{COOCH}_3 \end{array}$	
Per cent		Found
Cl. -----	19.43	19.58

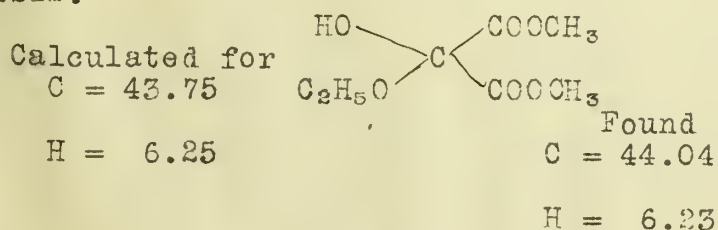
# ACTION OF ETHYL ALCOHOL ON THE CHLOR-TARTRONIC ESTER:

In order to prove the structure of the substance .42 cc.



of ethyl alcohol was added to 1.5046 grams of the pure product in a closed flask; heat was generated, and hydrochloric acid gas was formed under pressure. It liquified and from the liquid product a new substance quickly crystallized out in bunches of flat crystal plates. After the hydrochloric acid gas had been driven from the bottle by dry carbon dioxide gas, the product was pulverized and washed in sodium dried ether. After standing in a dessicator over night, it had a melting point of  $58^{\circ}$ . It was recrystallized from absolute alcohol, washed from ether, dried and analyzed.

ANALYSIS:



This product is identical in properties with the ethoxy body mentioned above.

PROPERTIES: The chlor-tartronic ester has a low melting point, is extremely unstable, and passes over quickly to the crystalline <sup>methyl</sup> dihydroxymalonate in moist air. It dissociates in certain dry organic solvents as ligroin and ether, as shown by the green color of the solution, while by others it is not dissociated. It is easily soluble in benzene and acetic ether, and fairly soluble in ligroin.

ANILINE ON THE CHLOR-TARTRONIC ESTER: When aniline is added to a solution of the chloride<sup>2</sup> of the methyl oxo-malonate, heat is generated and hydrochloric gas is evolved. The





solution turns yellow and, when the action is complete, a sticky, dark brown, gummy substance results. When allowed to stand for several days a mass of green crystals formed. These crystals, when treated with water, gave a mustard-yellow product, insoluble in ether and water. It was not further studied.

ACTION OF HYDROBROMIC ACID GAS ON THE KETONE ESTER:

Hydrobromic acid gas, which was dried by running first through a flask containing red phosphorus on glass wool, then through a tube, one-half of which was filled with anthracene and the other half with phosphorus pentoxide, was run into a small quantity of the ketone ester. The color gradually disappeared as the substance thickened. It was then cooled in a freezing mixture and little balls of crystals formed slowly. The crystals melted with the warmth of the hand and turned brown, due to liberation of bromine. The crystals form in bunches of prisms. They liberate hydrobromic acid when exposed to the air, are easily soluble in dry ether and fairly soluble in benzene. When heated, hydrobromic acid comes off and the ketone is formed. The bromotartronic ester has not been analyzed, but the method of formation, its reactions and general behavior, leave no doubt but that it has an analogous structure to that of the chlor-tartronic ester.

ACTION OF HYDRIODIC ACID GAS ON THE KETONE ESTER: Hydriodic acid gas, which was dried by running through a flask



containing red phosphorus and a tube containing phosphorus pentoxide, was run into chilled ketone ester for some time. The ketone became a lighter yellow and thinner. A few crystals formed at the neck and shoulder of the flask, and the liquid became darker and finally changed to purple-black. The crystals were indistinct, granular bunches which did not melt at the temperature of the room. When exposed to the light, they decompose and give off iodine. Later the crystals appear to be octohedrons and, when the bottle containing them was opened, no hydriodic fumes were given off. Some iodine had separated from the liquid and crystallized. The action of the haloid acids on the ketone ester appears to give a new class of compounds, having the haloid and hydroxyl groups on the same carbon atom.

Laboratory of Organic Chemistry,  
University of Illinois,

June 1st, 1908.

F. Grace C. Spencer,

In

Conjunction with

Dr. R. S. Curtiss.









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